

Thermal and UV photo-induced decomposition of azomethane on Rh(111)[†]

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Received 15th May 2000, Accepted 25th July 2000

Published on the Web 29th August 2000

The thermal and UV photo-induced decomposition of azomethane, $\text{CH}_3\text{N}=\text{NCH}_3$, was investigated by means of reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption spectroscopy (TPD). The RAIRS data revealed that azomethane adsorbs in the *trans*-configuration mode on Rh(111) at 90 K. During thermal treatment, azomethane decomposes exclusively by N–N bond scission, yielding H_2 , N_2 , C_2N_2 and traces of HCN. Upon UV irradiation at 90 K, adsorbed azomethane undergoes tautomerization, forming formaldehyde methylhydrazone, $\text{CH}_3\text{NHN}=\text{CH}_2$. The important features of the post-irradiation TPD spectra are the significant suppression of C_2N_2 and N_2 formation, and the appearance of the new products methylamine (CH_3NH_2) and CH_4 . C–N bond scission also occurred in the illuminated chemisorbed layer at 90 K.

1 Introduction

Azomethane ($\text{CH}_3\text{N}=\text{NCH}_3$) is an interesting molecule. Its thermal decomposition in the gas phase produces CH_3 radicals and N_2 by C–N bond cleavage.¹ This provides a convenient method for the preparation of CH_3 adsorbed on solid surfaces and study of its surface chemistry. On most metal surfaces, however, the primary process is the rupture of the N–N bond.^{2–7} It appears that the bonding of azomethane on certain surfaces allows a new decomposition pathway. C–N bond dissociation is induced by electronic excitation, such as the electron-induced decomposition of azomethane on Ag(111)⁸ and the UV photolysis of azomethane condensed on Pd(111).⁹ A study of the interactions of C_2N_2 with metal surfaces, demonstrated that the behaviour of Rh towards the CN group is basically different from that of Ag, Cu and Ni, as at high temperature it induces C–N bond cleavage to give adsorbed N and C.¹⁰ Rh also exhibits outstanding reactivity as compared to Cu in C–N bond breaking in the NCO surface complex.^{11–13}

In the light of the above findings, it appeared interesting to explore whether the high reactivity of Rh(111) towards the C–N bond is also exhibited in the decomposition of azomethane. A recent high-resolution electron energy loss spectroscopy (HREELS) study found that azomethane adsorbs molecularly in the *trans*-configuration on Rh(111) at 100 K, and dissociates exclusively *via* N–N bond scission above 300 K.¹⁴ Preadsorbed oxygen inhibits N=N bond breaking, leading to the C–N bond dissociation.¹⁴ The present paper reports on the use of combined RAIRS (with its better resolution) and TPD to acquire more information on the adsorption modes at 90 K, and on the bond rearrangement on a clean surface in the low-temperature range. It was found that UV light illumination alters the adsorption mode and chemistry of azomethane on Rh(111).

2 Experimental

The experiments were performed in a two-level UHV system with a background pressure of 5×10^{-10} mbar. The lower part of the chamber had facilities for Auger electron spectroscopy (AES) and TPD. The upper part was equipped with a single-beam Fourier-transform IR spectrometer (Mattson Research Series), which was used for the RAIRS experiments. All IR spectra were averaged over 512 scans using an MCT detector at $2\text{--}4\text{ cm}^{-1}$ resolution. Sample spectra were related to a background taken immediately after the sample scan by flashing the crystal to 1300 K. The scan was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1–2 kV, 1×10^{-4} Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel–alumel thermocouple. The typical heating rate for TPD was 4 K s^{-1} . Azomethane was synthesized according to the procedure described by Renaud and Leitch.¹⁵ The product was purified by several freeze–pump–thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H_2O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. Exposures were controlled by keeping the reservoir pressure constant and varying the dosing time. The absolute exposures in Langmuir are not known; thus relative exposures are therefore given as dosing times.

Adsorbate-covered surfaces were irradiated, through a UV-grade quartz window, with a 100 W high-pressure Hg arc lamp (Photon Technology Inc). The maximum photon energy at the sample was not greater than 5.4 eV (the onset of UV intensity from the Hg arc lamp). The incident power flux delivered to the crystal at full arc was about 100 mW cm^{-2} .

[†] Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b0/b003846f/>

The temperature rise of the crystal during irradiation did not exceed 5 K.

3 Results and discussion

3.1 Thermal chemistry of azomethane

The adsorption of azomethane on Rh(111) was performed at 90 K. The following gaseous products were detected by TPD measurements: azomethane (58 u), H_2 (2 u), N_2 (14 u) and C_2N_2 (52 u) (Fig. 1). Trace signals were detected at 27 u in the range 250–500 K. These weak signals can probably be attributed to the formation of HCN. Attempts were made to identify CH_4 , C_2H_6 , C_2H_4 and CH_3NH_2 (31 u), but without any positive results. The same product distribution was observed by Bol *et al.*¹⁴ In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that gave no multilayer peak. H_2 evolved in three well separated desorption peaks between 270 and 450 K. This complex behaviour differs from that following H_2 adsorption on clean Rh(111)¹⁶ and can be attributed to the decomposition of different fragments NCH_x . N_2 desorbed only above 700 K, with a $T_p = 795$ K. A previous study indicated that the N_2 molecularly adsorbed on Rh(111) desorbs at 160 K.¹⁷ The associative adsorption of N atoms (produced in a high-frequency discharge tube) occurred in a second-order process, with peak temperatures in the range 690–850 K.¹⁸ C_2N_2 desorption was not detected at very low exposures, its desorption started when chemisorbed azomethane was also revealed by TPD. CN recombination, as the reaction rate-determining step, was observed with $T_p = 695$ K, which corresponds to associative desorption of CN groups.¹⁰ Some very weak signals for HCN

were observed between 220 and 550 K. All these TPD results, and especially the absence of CH_4 from the desorbing products, suggest that the N–N bond rupture is exclusive and C–N bond dissociation does not occur.

Coverage-dependent IR spectra of adsorbed azomethane are displayed in Fig. 2. At submonolayer coverages, peaks were identified at 1007, 1445, 2915 and 2972 cm^{-1} . An increase of the azomethane exposure intensified these bands, produced a new band at 1386 cm^{-1} , and caused the splitting of the band at 1445 cm^{-1} into two bands, at 1438 and 1454 cm^{-1} . When multilayers were present, peaks were seen at 1003, 1375, 1386, 1438, 1454, 2851, 2915, 2962 and 2976 cm^{-1} . These multilayer features correspond well to those characteristic of solid azomethane in the *trans*-form (Table 1). It is important that there was no indication of any IR band due to an N=N vibration in the range of 1500–1600 cm^{-1} ; such bands were observed for *cis*-azomethane.^{2,5} There was a very strong band characteristic of the *trans*-isomer at 2915 cm^{-1} . We observed no vibration at 2999–3008 cm^{-1} which was found for the *cis*-form. Accordingly, the structure of azomethane on Rh(111) at 90 K is different from that observed for Pt(111) and Mo(100), where *trans*-azomethane converted to *cis*-azomethane upon adsorption.^{2,5}

To gain more information on the surface events, the adsorbed layer was gradually heated to higher temperatures and the IR spectra were recorded. A strong attenuation of all IR peaks characteristic of molecularly adsorbed azomethane was observed at 110–140 K, due to the desorption of azomethane and its transformation to other surface species (Fig. 3). No sign of azomethane was observed above 150 K. In the CH-stretching region, only a barely detectable peak was observed at 2920–2925 cm^{-1} (not shown). Above 250 K, there was no vibration in this frequency range. The most informative changes occurred in the low-frequency range. Above 250 K two strong vibrations dominate at 1356 and 1398 cm^{-1} , which can be attributed to the deformation bands of CH_x in the species $N-CH_x$. These bands have not yet been clearly identified. It is necessary to consider the presence of the perturbed fragment C–N which, depending on the adsorption mode, can give IR bands in the range 1300–1400 cm^{-1} .²¹ In this form the order of the CN bond is less than two. If it is accepted that azomethane dissociates thermally by N=N bond

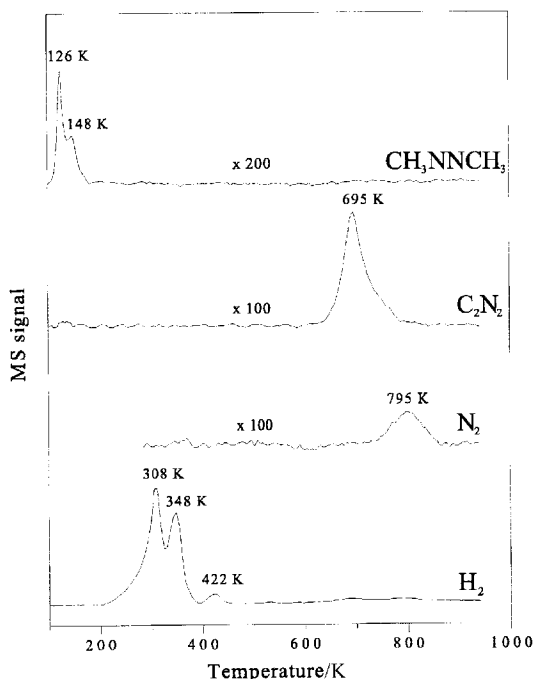


Fig. 1 TPD spectra following azomethane adsorption on Rh(111) at 90 K. The dosing time was 360 s (2 ML). Heating rate was 4 K s^{-1} .

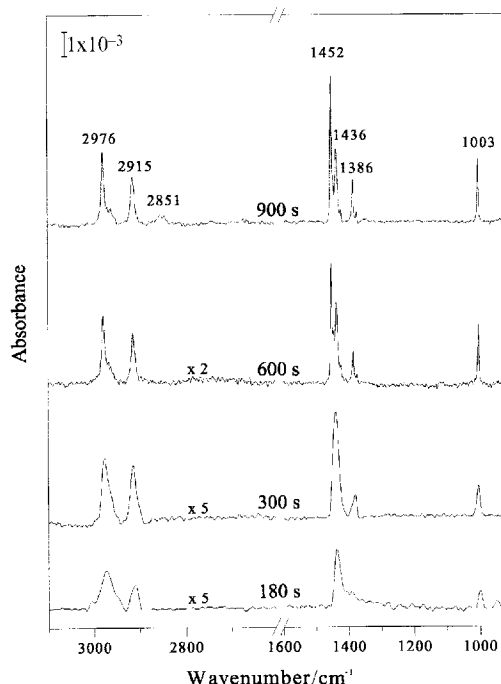


Fig. 2 RAIR spectra showing the exposure dependence of azomethane on Rh(111) at 90 K.

Table 1 Frequencies (cm^{-1}) and assignments of the fundamentals of azomethane adsorbed on different transition metal surfaces, and solid azomethane

<i>Trans</i> -solid ¹⁹	<i>Cis</i> -solid ²⁰	Pt(111) mono ²	Mo(110) mono ⁵	Rh(111) mono	Rh(111) multilayer	Assignment
2975	3008	2999		2972	2976	$\nu_a(\text{C-H})$
2966	2960				2962	
2911				2915	2915	$\nu_s(\text{C-H})$
2847	2840		2882		2851	$2\delta_a(\text{CH}_3)$
			2836			$2\delta_s(\text{CH}_3)$
			2752			
	1556	1540	1570			$\nu(\text{N=N})$
	1545		HREELS			
1450	1472	1415	1432	1445	1454	$2\delta_a(\text{CH}_2)$
1443	1466				1438	
1433	1437					
1421						
1386	1369	1315		1381	1386	$\delta(\text{HCN})$
1373	1361					and
1330	1349					$\delta(\text{CH}_2)$
1112	1178					$\delta(\text{HCN})$
1001	1098	1010	1080	1007	1003	$\nu(\text{C-N})$

breaking (based on our TPD results), the presence of species N-CH_3 may be assumed. In this case, a characteristic N-C vibration should be detected at around 1000 cm^{-1} . The absence of this band suggests that this species is inclined toward the surface, and perhaps partially hydrogenated on the N side, resulting in species H-N-CH_3 adsorbed *via* the N lone pair. The bands at 1356 and 1398 cm^{-1} disappeared above $260\text{--}285 \text{ K}$, and a new band appeared at 1408 cm^{-1} ; this was present up to 350 K , from which temperature a new peak developed at 1564 cm^{-1} . This band disappeared at around $440\text{--}450 \text{ K}$. At this stage, we are inclined to think that the species $(\text{H})\text{-N-CH}_x$ decomposes or is transformed to a transient adsorption form of C-NH_x . The band at 1408 cm^{-1} is possibly due to H-C-NH , while that at 1564 cm^{-1} corresponds to the deformation of NH_2 in C-NH_2 , the aminomethylidyne species. C-NH_2 was also observed during azomethane decomposition on Pt(111) .² This surface species

can likewise be also easily detected by RAIRS in the interaction between the adsorbed CN group and hydrogen.²² The $\delta(\text{NH}_2)$ was observed at 1567 cm^{-1} , while the $\nu(\text{CN})$ appeared at 1323 cm^{-1} with intensity lower by a factor of 5 on Pt(111) .²² C-NH_2 should be in equilibrium with CN in the $300\text{--}450 \text{ K}$ range, based on the relative intensities of the deformation and the stretching vibrations of C-NH_2 . C-NH_2 decomposes above 450 K , as indicated by the disappearance of the band at 1564 cm^{-1} . No vibration could be detected above this temperature, as the decomposition product ($\text{C}\equiv\text{N}$) is probably bound parallel to the surface, and is therefore invisible to RAIRS on the basis of surface selection rules. The thermally induced decomposition mechanism of azomethane is depicted in Fig. 6A (below).

3.2 Photo-induced chemistry of azomethane

This section deals with photon-driven chemistry, which occurs mainly in the first layer. The most informative TPD products at monolayer coverage as a function of irradiation time are displayed in Fig. 4. The thermal desorption characteristics of the parent molecule did not change in response to UV light, but the amount of azomethane slightly decreased with increasing irradiation time. At higher coverages of azomethane, the effect of UV illumination could be observed by following the molecular traces of the parent molecule at 58 and 43 u. The peaks characteristic of the desorption of azomethane from the multilayer disappeared and a new desorption feature developed at $T_p = 135 \text{ K}$; this is attributed to a new desorption form with slightly altered chemical behaviour.

The appearance of a new species is also visible in the RAIRS spectra taken after UV irradiation (Fig. 5). At both monolayer and multilayer coverages new bands developed at $2930, 2878, 2854, 1720, 1471, 1350$ and 1120 cm^{-1} after a relatively long illumination time. The appearance of new peaks in the C-H -stretching ($2950\text{--}2820 \text{ cm}^{-1}$) and the deformation ($1300\text{--}1500 \text{ cm}^{-1}$) regions indicates some transformation in the terminal CH_3 groups. The band at 1120 cm^{-1} , assigned to $\nu(\text{N-N})$,² clearly reflects the tautomerization of azomethane to formaldehyde methylhydrazone. A weak signal could also be detected at 1720 cm^{-1} , attributed to the $\nu(\text{C=N})$ stretching vibration, but unfortunately the $\nu(\text{N-H})$ and $\rho(\text{N-H})$ vibrations (characteristic features of the tautomer) could not be observed above 3300 cm^{-1} and below 900 cm^{-1} because of the low sensitivity of our spectrometer in these regions.

One of the most important effects of irradiation is the appearance of CH_3NH_2 in the TPD spectrum at 31 u at $T_p =$

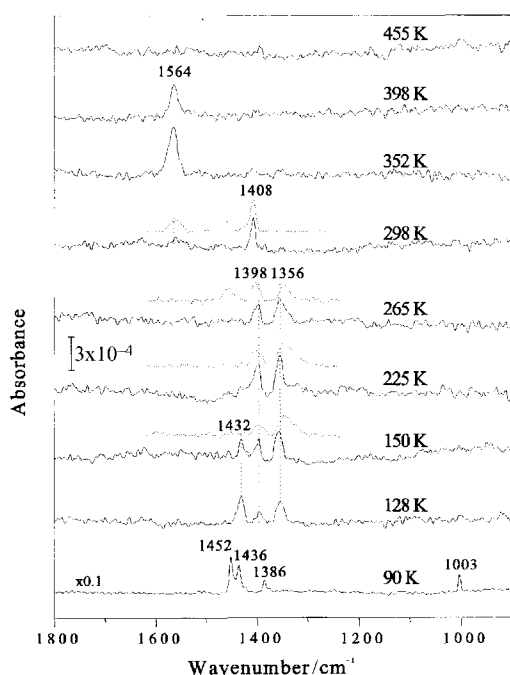


Fig. 3 RAIR spectra as a function of annealing temperature following an initial azomethane exposure of 600 s (3 ML) at 90 K . The dashed curves denote the adsorbate covered surface after illumination and annealed to the indicated temperatures.

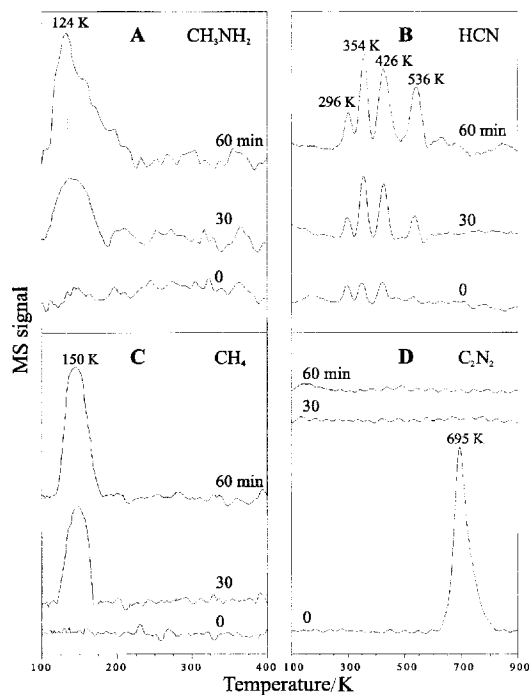


Fig. 4 TPD spectra for 1 ML (180 s dose) azomethane adsorbed on Rh(111) as a function of increasing irradiation time. The sample was irradiated at 90 K.

124 K, with a high-temperature tailing. This feature was not observed in dark experiments; its intensity increased in response to UV photon exposure (Fig. 4A). The peak temperature of CH_3NH_2 ($T_p = 124$ K) is in good agreement with that found in a previous study of CH_3NH_2 adsorption on Rh(111) by Schmidt *et al.*²³ The low temperature of CH_3NH_2 desorption indicates a desorption-limited process, i.e. the CH_3NH_2 molecule is produced by illumination or by direct decomposition of the tautomer on heating to 120 K. The presence of the IR band at 1471 cm^{-1} could be assigned to

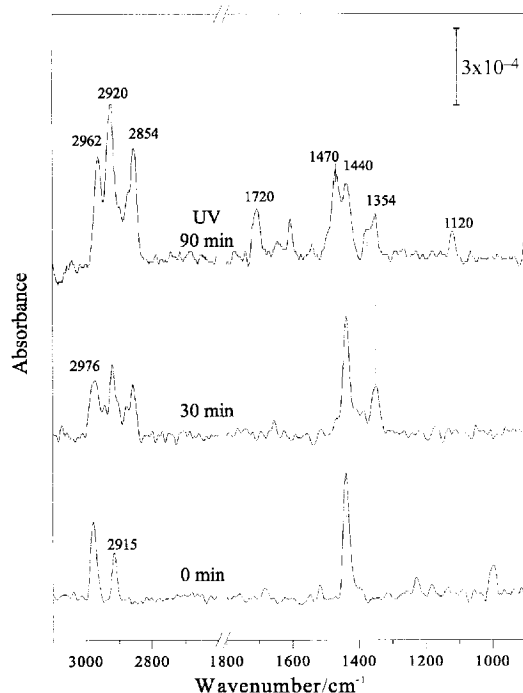


Fig. 5 RAIR spectra for 1 ML (180 s dose) azomethane adsorbed on Rh(111) as a function of irradiation time. The sample was irradiated at 90 K.

$\delta_a(\text{CH}_3)$ of CH_3NH_2 , and the other observed bands are also close to the fundamentals of CH_3NH_2 ,² but the close similarity to those of azomethane makes it impossible to draw the conclusion that CH_3NH_2 is present at 90 K as an effect of illumination. The formation of CH_3NH_2 necessitates a lower temperature than 124 K (desorption of the molecule), as, without illumination, we could not detect CH_3NH_2 either adsorbed or in the gas phase. Above this temperature the dehydrogenation of the presumed intermediate ($\text{HN}-\text{CH}_3$) to NCH_2 is faster than the hydrogenation process, explaining the absence of CH_3NH_2 in the dark experiments.

C_2N_2 which was the main product in dark experiments, could not be observed even after a short irradiation time (Fig. 4D). The extent of HCN formation, which was detected only in traces without irradiation, markedly increased in response to UV illumination. HCN desorption peaks were observed at $T_p = 296, 354, 426$ and 536 K. The N_2 and H_2 TPD features remained the same as those observed without irradiation; however, their amounts decreased slightly. The disappearance of C_2N_2 desorption can be explained by the reduced amount of CN groups. A large amount of azomethane is tautomerized to the hydrazone form and/or dissociates into CH_3NH_2 ; most of the latter desorbs without further dissociation to CN. At low coverages, CN groups decompose to C and N instead of undergoing recombination at elevated temperature.¹⁰

The rather complicated structure of the desorption of HCN and H_2 is not yet completely understood, but should be controlled by the surface concentrations of H and CN-containing species and by the reactions between them.

The other significant effect of irradiation is the appearance of CH_4 in the desorption products, as can be seen in Fig. 4C. The amount of CH_4 increased with the illumination time, indicating a certain extent of C–N bond breaking as in the gas-phase photochemical mechanism of azomethane.²⁴ The first step in CH_4 evolution is the formation of an adsorbed CH_3 group, and consequently the stretching vibration at 2920 cm^{-1} increases in Fig. 5. In agreement with the former measurements, adsorbed CH_3 is self-hydrogenated into CH_4 , which is desorbed at a peak temperature of 150 K.²⁵ During irradiation, a small rise in the N_2 signal is observed isothermally, demonstrating photolytic decomposition at 90 K. Yates *et al.* found that only *trans*-azomethane produces CH_4 photolytically on Pd(111).⁹ As we could also detect CH_4 desorption after illumination of the first layer, this confirms the presence of the *trans*-form in the monolayer on Rh(111), which was not found either on Pd(111),⁴ Pt(111)² or Mo(110).⁵

Some changes as compared to dark experiments could be seen in the RAIR spectra after annealing of the illuminated layer. There is a broader band near 1350 cm^{-1} , which is shifted to lower values and consists of two poorly resolved peaks. The FWHM of this feature becomes smaller above 265 K, and disappears by 300 K. The band at 1408 cm^{-1} appears at much lower temperature (150 K) after illumination. It is the most intense feature in this region in the range 200–300 K, while the band at 1395 cm^{-1} could not be detected above 255 K. In dark experiments, the above-mentioned peaks appeared and disappeared in reverse order, as can be seen in Fig. 3 (the dashed lines denote the illuminated sample). We can conclude from this observation that the thermal dissociation of the tautomer form is slightly different to that of the parent azomethane. The dissociation of the N–N bond in the tautomer forms $\text{HN}-\text{CH}_3$ and $\text{N}=\text{CH}_2$. The latter or its tautomer form ($\text{HN}=\text{CH}$) is probably responsible for the band at 1408 cm^{-1} ,²¹ which appeared at much higher temperature (above 250 K) without UV irradiation. $\text{NH}-\text{CH}_3$ is partially dehydrogenated, presumably to $(\text{H})\text{N}=\text{CH}_2$, as indicated by the disappearance of the band at 1398 cm^{-1} and the enhancement of that at 1408 cm^{-1} . Above 300 K, the fragment $(\text{H})\text{N}=\text{CH}_2$ is transformed to CNH_2 , as in dark experiments. The only difference between the findings of illuminated and dark experi-

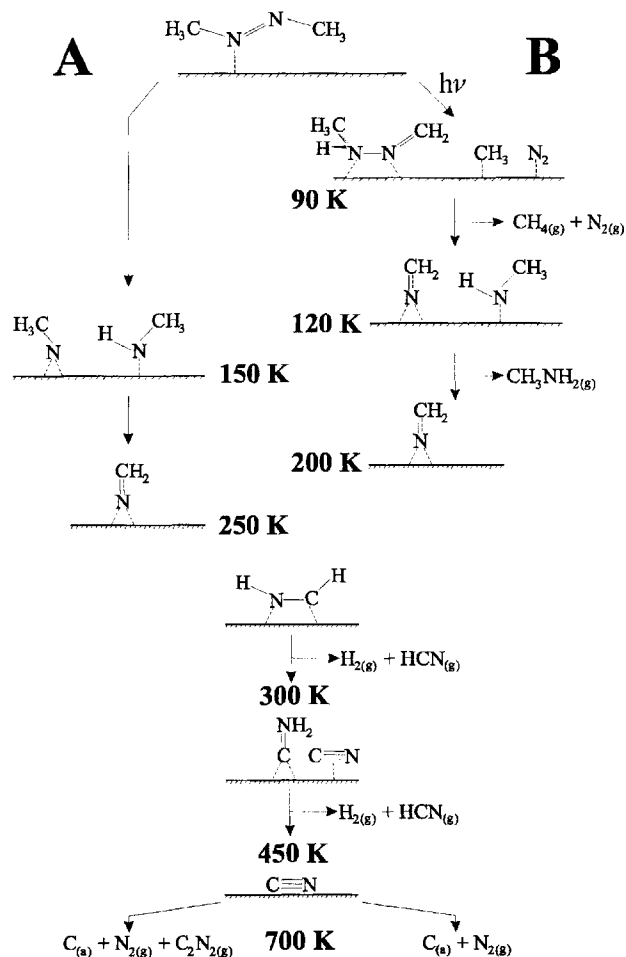


Fig. 6 Scheme for the adsorption and decomposition of azomethane on Rh(111): A, thermal-induced; B, photo-initiated processes.

ments above 300 K is that smaller amounts of CNH_2 and CN were produced after illumination, as indicated by the absence of C_2N_2 from the TPD products. The transformations induced by UV irradiation and annealing are displayed in Fig. 6B. We may assume that the first step in the surface photochemical process is the photo-induced *trans-cis* isomerization, which occurred in the homogeneous condensed phase.^{26,27} As discussed above, there are significant IR spectral differences between the *trans*- and *cis*-forms of azomethane. We could not detect any signal characteristic of the *cis*-form. We therefore believe that UV illumination causes a transformation from the *trans*-isomer to formaldehyde methylhydrazone via the tautomerization process; this does not hold for direct photo-decomposition, which leads to N–C bond breaking.

4 Conclusions

1. This RAIRS study revealed that azomethane is adsorbed molecularly in the *trans*-configuration on Rh(111) at 90 K and

dissociates thermally exclusively via N–N bond scission. The decomposition products are N_2 , H_2 , C_2N_2 and traces of HCN .

2. Aminomethyldiene, CNH_2 , is one of the surface intermediates in the transformation to the CN group. A proportion of the CN groups recombine to C_2N_2 , and the remainder decompose. N_2 is formed by recombination of N atoms.

3. The adsorbed *trans*-azomethane tautomerizes to formaldehyde methylhydrazone during UV illumination at 90 K. Photo-induced *trans-cis* transition was not observed. Illumination enhanced C–N bond breaking.

4. UV irradiation significantly altered the product distribution during thermal desorption. New products, CH_3NH_2 and CH_4 , were formed and C_2N_2 evolution ceased.

Acknowledgements

This work was supported by the Hungarian Academy of Sciences and OTKA grant T32040.

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